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High-Performance Fibers to Imidazole and Derivatives

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Contents

Cross References

High-Pressure Technology, treated in B4
High-Tech Ceramics → Ceramics, Advanced Structural Products
High-Temperature Composites → Composite Materials; → Metallic-Matrix Composites
High-Temperature Fibers → High-Performance Fibers
High Temperature Plastics → Specialty Plastics
High-Tenacity Fibers → High-Performance Fibers
Histamine Antagonists → Antiallergic Agents; Antacids and Peptic Ulcer Treatment
Histidine → Amino Acids
Hollow-Fiber Membranes → Membranes and Membrane Separation
Holmium → Rare Earth Elements
Hydroboranation → Boron Compounds
Hydrobromic Acid → Bromine Compounds
Hydrocarbon Oxidation → Oxidation
Hydrocarbon Resins → Resins, Synthetic
Hydroformylation → Oxo Synthesis
Hydrogen Bromide → Bromine Compounds
Hydrogen Chloride → Hydrochloric Acid
Hydrogen Cyanide → Cyano Compounds
Hydrogen Economy → Hydrogen
Hydrogen Fluoride → Fluorine Compounds, Inorganic
Hydrogen Iodide → Iodine
Hydrogen Selenide → Selenium and Selenium Compounds
Hydrogen Storage Alloys → Hydrides
Hydrometallurgy → Metallurgy
Hydroxyanthraquinones → Anthraquinone Dyes
Hydroxybenzaldehyes → Benzaldehyde
Hydroxyhydroquinone → Phenol Derivatives
Hypochlorous Acid → Chlorine Oxides and Chlorine Oxygen Acids
Hypoglycemic Drugs → Antidiabetic Drugs
Hydrophosphorus Acid → Phosphorus Compounds, Inorganic
Illites → Clays

cobalt- or rhodium-phosphin complexes are used.

Propen is the olefin mostly used. The oxo-products are converted to alcohols, carboxylic acids, aldol-condensation products, and primary amines. About 20 commercial processes are state of the art. An excellent review is given in [8.41] (see → Oxo Synthesis).

Homologation. Under the reaction conditions of the hydroformylation alcohols and aldehydes react with carbon monoxide–hydrogen under elongation of the chain by one CH_2- unit

$$R-CH_2-OH + CO/H_2 \rightarrow R-CH_2-CH_2-OH + H_2O$$

Homologation has been performed with a number of alcohols, the production of ethanol from methanol has been most intensively investigated. The homologation is not used industrially because of the many side reactions which take place [8.42].

Synthesis Gas as Chemical Feedstock. Hydrogen–carbon monoxide mixtures, hydrogen alone, and their primary product methanol are important feedstocks for the chemical industry. Nowadays, ethylene which is produced from propane, ethane, naphtha, or gas oil is the most important feedstock for the production of industrial organic chemicals in the chemical industry. Bascially, it is, however, possible to obtain these compounds from synthesis gas thus changing the feedstock basis to coal (see Fig. 100).

8.1.5. Hydrogen in Organic Synthesis

Hydrogen is required for the production of chemicals and intermediates in organic chemistry. A large number of hydrogenations or reductions are carried out on a technical scale (→ Hydrogenation and Dehydrogenation).

Activated and nonactivated double and triple bonds in olefins and acetylenes can be easily partially or totally hydrogenated, whereas the hydrogenation of aromatic and heterocyclic bonds requires more energetic conditions. Functional groups, such as carbonyl, nitro, nitroso, and nitrile groups, can also be hydrogenated.

The reaction conditions are dictated by equilibrium (65). The reactions are exothermal and run in the presence of a catalyst.

$$A + nH_2 \longrightarrow BH_{2n} \qquad (65)$$

Directions for carrying out catalytic hydrogenations on a laboratory or industrial scale are given in [8.43]. Summaries of hydrogenation reactions are given in [8.44] and [8.45]. Hydrogenation catalysts are metals of groups 8–10 of the periodic system (see front matter of this volume), e.g., Raney nickel, as well as copper and molybdenum. In particular the noble metals (Pt, Pd), are highly-active catalysts [8.46]. Homogeneous systems with molecularly dispersed catalysts in the solution, can be used for special synthesis problems (selective hydrogenation, asymmetric synthesis) but are at present of no great importance in commercial areas because of the frequently encountered difficulty to remove the catalyst from the reaction mixture. Table 40 gives an

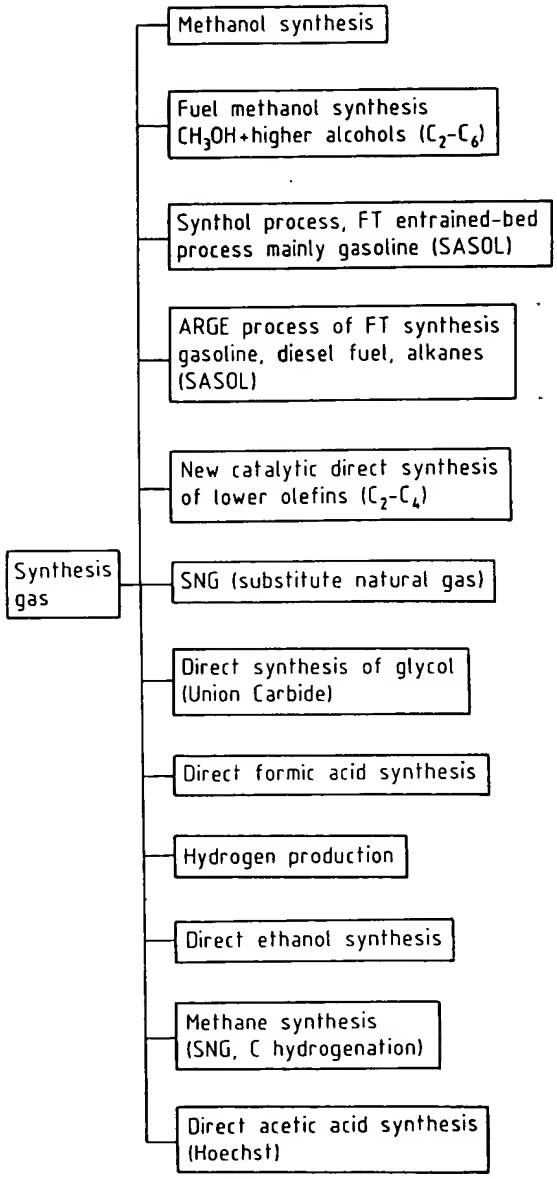


Figure 100. Synthesis gas as feedstock in the chemical industry

Table 40. Selection of important industrial hydrogenation reactions

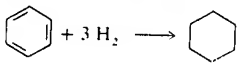
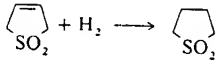
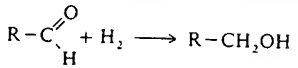
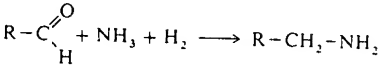
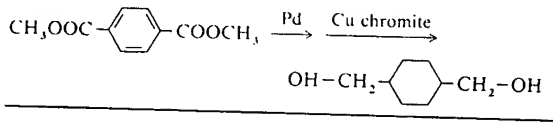
Reaction	Product	Process features	Uses
Hydrogenation of unsaturated hydrocarbons and aromatics			
	cyclohexane	middle pressure hydrogenation over Ni-/Pt-Li-Al_2O_3 catalyst in liquid phase (IFP, Mitsubishi) gas phase (UOP, DSM, Thoray, Houdry)	starting material for nylon production (cyclohexanone/ol, adipic acid, caprolactam), solvent
(analogous: cyclohexanol from phenol, cyclohexane carboxylic acid from benzoic acid)			
$CN-CH_2-CH=CH-CH_2-CN + H_2 \longrightarrow CN-(CH_2)_4-CN$	adiponitrile	Du Pont (300 °C), liquid phase hydrogenation 25 - 30 MPa/70 - 100 °C over Raney nickel	hexanediamine
$OH-CH_2-C\equiv C-CH_2OH + 2H_2 \longrightarrow OH-(CH_2)_4-OH$	butanediol	trickle bed, 20 MPa, 180–200 °C Ni catalyst with Cu-, Cr-promotors	polyesters, polyurethane-plasticizer component, solvent
	sulfolane	Shell process, 11 000 t/a	aromatics extraction solvents, sour gas, scrubbing agent
Selective hydrogenation as purification step during production of ethylene, propene, and butadiene			
Further processing of oxo-products			
	oxo-alcohols	gas phase hydrogenation at 2–0.3 MPa/115 °C, Ni catalyst sump phase hydrogenation, 8 MPa/115 °C Ni catalyst	components for solvents, plasticizers, detergents
(analogous: ethylhexanol from ethylhexanal)			
	primary amines	hydrogenation (up to 30 MPa, 25–130 °C), Raney nickel catalyst	
Hydrogenation of other ketones and aldehydes			
Maleic acid ⟶ butyrolactone ⟶ $OH-(CH_2)_4-OH$	butanediol	Mitsubishi, Kao Ind. (Japan) process	
	bis-(hydroxymethyl)-cyclohexane	two step Eastman-Kodak process	

Table 40. (continued)

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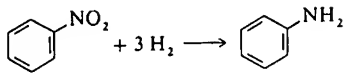
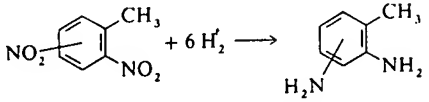
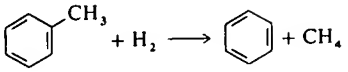
Reaction	Product	Process features	Uses
$CH_2=CH-C(=O)H + H_2 \longrightarrow CH_2=CH-CH_2OH$	allylalcohol	Degussa gas phase process (heterogenous catalysis)	starting material for glycerol, glycidol
2 Acetone $\longrightarrow$ mesityl oxide $\xrightarrow{\text{Pd zeolite}}$ $i\text{-Bu}-C(=O)-CH_3$	MIBK	hydrogenation at Pt–zeolites (modified one step processes)	(extraction) solvent
Fats, oils + $H_2 \longrightarrow R-CH_2-OH$	fatty alcohols	20–40 MPa/200–400 °C, catalysts of Adkins-type	
$R-O-CH_2CH_2-OH + HCHO + H_2 \rightarrow R-O-CH_2CH_2-OCH_3$	polyethylene-glycol ethers	new Hoechst process	sour gas scrubbing agent (Selexol)
Hydrogenation of N-compounds			
	aniline	fixed bed hydrogenation over NiS/CuS, 300–475 °C (Bayer, Allied, Lonza), fluidized bed hydrogenation, 5 MPa/100 °C over Cu catalyst (BASF, Cyanamid)	starting material for dyes, pharmaceuticals, isocyanate polymers, solvents
	diaminotoluenes	analogous to nitrobenzene reduction	
Nitriles + $H_2 \rightarrow$ primary amines	hexanediamine	5–15 MPa/60–130 °C over Raney Ni or Raney Co	starting material for fibers, sour gas scrubbing agent
Miscellaneous reactions			
	benzene	3–5 MPa/500–650 °C over $Cr_2O_3-Mo_2O_3-CoO$ catalyst (Houdry, UOP, Shell, BASF) 10–25 MPa/400–500 °C over $Pt-Al_2O_3-SiO_2$	50% of toluene production further processed to benzene
Xylene isomerization under H_2 partial pressure	o-/p-xylene	catalysts	terephthalic acid, phthalic acid

overview of commercially used hydrogenation reactions.

High-purity hydrogen is necessary for the partial or total hydrogenation of fats and oils (for the production of edible fats or for technical purposes). In fat hydrogenation the polyene, triene, and diene fatty acids in their glyceride form are selectively hydrogenated to the corresponding monoene acids.

The industrial production of sugar alcohols, such as sorbitol, xylitol or mannitol from the corresponding sugars is carried out by catalytic hydrogenation. Batch suspension processes using Raney nickel catalysts are mainly employed under reaction conditions of 120–150 °C and 3–7 MPa [8.47].

8.1.6. Hydrogen in Inorganic Synthesis

The catalytic hydrogenation of anthraquinone and its derivatives followed by their autoxidation to yield hydrogen peroxide is the basis of the commercially important process for hydrogen peroxide production (→ Hydrogen Peroxide, p. 447–456). Further important reactions in inorganic chemistry are the production of hydrochloric acid from hydrogen and chlorine (→ Hydrochloric Acid) and the hydroxylamine synthesis (→ Hydroxylamine).

8.2. Hydrogen in Metallurgy

Iron Metallurgy. To reduce iron ore, apart from coke (classical blast furnace process), other reducing agents can be used. For reduction a gas containing hydrogen, carbon monoxide, or mixtures of these is suitable. The reduction gas is produced by steam reforming or partial oxidation of fossil fuels. These *"direct reduction"* processes (→ Iron, **A14,** p. 554) yield sponge iron, which can be melted to give crude iron which is further processed to steel.

The leading direct reduction technologies are the Midrex, the HyL I, and the HyL III process with 90 % of the total capacity [8.48]. The hydrogen content of the reducing gas is ca. 40–65 vol % (Midrex, shaft furnace) and 75 vol % (HyL III, retorts). To fully utilize the reduction potential of the gas, carbon dioxide and water vapor are removed and the gas is recycled.

The use of *pure hydrogen* has advantages with respect to the reaction time, the degree of reduction and the texture of the reduced pellets [8.49], but the carbidizing reaction necessary for steel production cannot take place, so that reduction with pure hydrogen has not been able to establish itself.

Nonferrous Metallurgy. Hydrogen is employed as reducing agent and as utility in some powder metallurgy production processes. Table 41 shows the use of hydrogen during the production and handling of various nonferrous metals.

For recovery of copper from its sulfidic ores reduction with hydrogen in the presence of calcium oxide has been suggested [8.50]. The thermodynamically unfavorable position of the hydrogen reduction reaction on metal sulfides is improved by the removal of the developing hydrogen sulfide (as CaS) from the equilibrium mixture.

8.3. Other Uses

Use of the High Temperature of the Oxyhydrogen Flame. The combustion of a stoichiometrical hydrogen–oxygen mixture leads to flame temperatures in the range of 3000–3500 K. Such flames can be used for:

Table 41. Use of hydrogen in the nonferrous metallurgy

Metal	Unit operation	Product
Copper	reduction of copper salt solutions under pressure	Cu powder
Nickel	selective reduction during cobalt production	Ni powder
Cobalt	reduction of aqueous cobalt salt solutions under pressure (4 MPa, 175 °C)	Co powder
Molybdenum, tungsten	reduction of the oxides or molybdates and tungstenates	Mo, W powder
Tantalum	reduction of tantalum chloride, $TaCl_5$, in hydrogen plasma	Ta hydride, Ta powder
Germanium	reduction of germanium tetroxide, GeO_4, at 650 °C	Ge powder for further processing in zone melting
Uranium	reduction of the higher uranium oxides at 650 °C	UO_2